
Synthesis and characterization of the peroxy complexes of uranium (VI) containing organic acids and amine bases ligands

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Abstract: Several new peroxy complexes of U(VI) have been synthesized and characterized by element analyses and various physico-chemical techniques. A number of organic and amine ligands were used to form the complexes having compositions, $[UO(O_2)amH_2L]$, where, $[amH=$ amino acids, such as glycine, phenylalanine, leucine ; $L=$ ligands such as pyridine, 2-picoline, 4-picoline, quinoline, iso-quinoline. The analytical data are in good agreement with the proposed empirical formulae of the U(VI) complexes. The molar conductance values indicate all the complexes of U(VI) are non-electrolyte in DMF revealing that the anions are covalently bonded in all the cases. The disappearance of the $\nu(O-H)$ mode observed in the free amino acid molecule clearly indicate the loss of protons from O-H group coordination, revealing that acids are dinegative bidentate ligand coordinating through the carboxylate anion. The characteristic $\nu_1(O-O)$ mode of the complexes appeared in the region 842-916 cm^{-1} , indicating that the dioxygen moieties are bonded on "side-on" fashion with the U(VI). The magnetic moment values indicated that these complexes were diamagnetic in nature suggesting no changes in the oxidation states of the metal ions upon complexation. These data also consistent with eight fold coordination of U(VI). The electronic spectral data of the complexes showed bands in between 315-380 nm due to the charge transfer band only.

Keywords: Synthesis, Characterization, Peroxy Complexes, Uranium (VI)

1. Introduction

Metal peroxy complexes have been the object of intense investigation for the past several years, for a variety of reasons including their role as oxidation catalyst [1] and biochemical relevance [2]. They are widely used in stoichiometric as well as catalytic oxidation in organic and biochemistry [3], for example in the oxidation of thioanisole [4], methyl benzenes [5], tertiary amines, alkenes, alcohols [6], bromide [7] and also in olefin epoxidations [8]. Peroxy complexes of uranium are attracting interest as oxidants in organic synthesis [9]. As uranium somewhat resembles the group VIB elements, it was of interest to discover whether it would form analogous peroxy complexes which contain organic moieties. Various peroxy complexes of uranium have been reported with organic ligands [10]. The coordination number for metal chelates of UO_3 has been reported [11]. The chemistry of heteroligand peroxy-metallates possesses a fascinating and worthwhile area of investigation [12]. The synthesis of well defined heteroligand peroxy-metal complexes therefore is an

important prerequisite for a heuristic approach in this field of chemistry. It is imperative to note that in recent years a commendable progress has been made in this aspect of lighter metals and a good amount of newer information as well as materials has emerged thereof [13-15].

Studies on the peroxy complexes have received considerable attention due to their application in synthetic organic chemistry [16-20]. Peroxy complexes of transitional metals are sources of active oxygen atoms and many of these complexes can be used as efficient stoichiometric as well as catalytic oxidants for organic and inorganic substrate [19,20]. It has been observed that the reactivity of the peroxy complexes depend on the nature of other auxiliary ligands used. Peroxy complexes containing monodentate and bidentate auxiliary ligands were found to be undergoes oxygen transfer reactions [21-23], those containing tridentate and quadridentate ligands were inert towards oxidation reaction [24].

The present research deals with the synthesis and characterization of peroxy complexes of uranium (VI) with

some organic acids and amine bases ligands. The structures of ligands are given in scheme.

2. Materials and Methods

General method for the preparation of the complexes of the type $[U(O_2)(amH)_2L]NO_3$ [where amH= deprotonated glycine, alanine, phenylalanine and leucine; L= quinoline, isoquinoline, pyridine, 2-picoline or 4-picoline]

A solution of amH namely glycine (0.150g, 0.002 mol) or alanine (0.1782g, 0.002mol) or phenylalanine (0.330g, 0.002mol) or leucine (0.2623g, 0.002mol) in water (20 ml) was added with stirring to a solution of Uranyl nitrate (1.005g, 0.002 mol) in water (20 ml). A solution of 'L' (0.01 mol) in ethanol was then added with continuous stirring to the above mixture followed by the addition of 30% H_2O_2 (2 ml). The precipitate appeared which was filtered, washed several times successively with ethanol. It was then dried and stored in *Vacuo* over P_4O_{10} .

2.1. Reaction of the Complexes of 4 & 5 with Allyl Alcohol

Complexes 4 and 5 (0.002 mol) were suspended in 30 ml of THF and a stoichiometric amount of allyl alcohol was added. The mixture was added. The mixture was stirred under reflux at 60°C for 48 hours, but failed to produce any epoxy product, complexes 4, 5, 8 & 11 were recovered unchanged. Refluxing complexes 4 & 5 with allyl alcohol in a 1:1 molar ratio in THF medium in 48 hours also failed to produce any epoxy product.

2.2. Reaction of the Compounds 6 with Allyl Alcohol (Reaction A)

A stoichiometric amount of allyl alcohol was added to a suspension of complex 6 or 7 in THF (30ml). The mixture was stirred under reflux at 65°C for 36 hours. Microdistillation under reduced pressure (19mm Hg) yielded glycidol (75% yields) at 145-150°C. The glycidol was identified by means of its phenylurethan derivative, m.p. 58-60°C (m.p. 60°C) [25, 26].

2.3. Reaction of 1 and 3 Complexes with Triphenylphosphine (Reaction B)

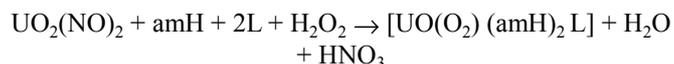
Triphenyl phosphine (1.321g, 0.005 mol) was dissolved in THF (50ml) which was reflux with an equimolar quantity of the complexes (0.005 mol) suspended in the same solvent (30 ml). The progress of the reaction was monitored using TLC indicating complete oxidation of triphenyl phosphine in 7 hours of reaction time. The solution was filtered and the residue was collected. The product was recovered from the filtrate and was identified as $OPPh_3$, m.p. 154-155°C (m.p. 157°C) [27].

Reaction of the compounds 2 with triphenylarsine (Reaction C): Triphenylarsine (0.90g, 0.005 mol) in THF (50ml) added to a suspension of above compounds in the same solvents (50ml). The mixture was refluxed for 60 hours. The progress of the reaction was monitored using TLC, indicates that triphenylarsine was converted completely into

triphenylarsine oxide. The reaction mixture was filtered and the residue was stored. Evaporation of the filtrate yielded the product, m.p. (m.p. 190-192°C) [27 -29].

3. Results and Discussion

The complexes were prepared from the reaction of the Uranyl nitrate with organic acids and amine bases. The reaction may be represented as follows:



Where, amH= deprotonated glycine, alanine, phenylalanine and leucine; L= quinoline, isoquinoline, pyridine, 2-picoline or 4-picoline.

Elemental analysis and conductivity measurement: The analytical data and their physical properties of the complexes are shown in Tables 1 and 2 respectively. The analytical data are in good agreement with the proposed empirical formulae of the present complexes. Their structures have been proposed on the basis of conductivity and magnetic measurements (Table 2) and electronic spectral data (Table 4).

The molar conductance of 10^{-3} M solutions of the complexes in DMSO was measured at 30°C. The molar conductance values (Table 2) indicate all the complexes are non-electrolytes in DMF revealing that the anions are covalently bonded in all the cases.

3.1. IR Studies

Infrared spectral data are represented in table 3 and figures 1 & 2. The complexes display $\nu(C=O)$ bands at $\sim 1683cm^{-1}$ and $\nu(C-O)$ bands at $\sim 1575cm^{-1}$ significantly lower than the values of amino acid ($\sim 1690cm^{-1}$ and $\sim 1586cm^{-1}$). These indicate the coordination of amino acid through their carboxylate anion. The uranium (VI) complexes display $\nu(M=O)$ modes in the region $903-994cm^{-1}$. Further, the presence of M-N and in the complexes are evident from the appearance of $\nu(M-N)$ modes at $423-464cm^{-1}$ in the spectra of the complexes [26,30]. The complexes display $\nu(N-H)$ modes in the region of $3105-3316cm^{-1}$.

The metal peroxo grouping gives rise to three IR active vibrational modes. These are predominantly O-O stretching ν_1 , the symmetric M-O stretch ν_2 and the antisymmetric M-O stretch ν_3 . The characteristics of $\nu_1(O-O)$ modes of the complexes appear at $797-882cm^{-1}$. It is observed that the ν_1 mode decreases with the increase atomic number of the metal in particular group. In the present complexes, the ν_3 and ν_2 modes appear at $600-668cm^{-1}$ and $510-599cm^{-1}$ respectively.

3.2. Magnetic Moment and Electronic Spectra

The observed values of effective magnetic moment (μ_{eff}) at room temperature are given in Table 2. The magnetic moment values of dioxouranium (VI) complexes (-0.23 to 0.46 B.M.) indicated that these complexes are diamagnetic in nature and this revealed that there was no change in the oxidation states of the metal ions upon complex formation.

The electronic spectral data (Table 4) of the complexes 1-6 transfers band only [31]. showed bands between 230-370 nm regions due to the charge

Table 1. Analytical data and physical properties of U(VI) complexes.

Complex No.	Complexes	Yield %	M%	C%	H%	N%
1	[UO(O ₂)(gly) ₂ (py)]	65	46.24 (46.39)	21.00 (21.05)	2.43 (2.59)	8.06 (8.19)
2	[UO(O ₂)(gly) ₂ (2-pic)]	67	45.02 (45.15)	22.81 (22.76)	2.68 (2.85)	7.78 (7.97)
3	[UO(O ₂)(gly) ₂ (4-pic)]	60	46.02 (46.23)	22.07 (22.24)	2.43 (2.59)	7.48 (7.64)
4	[UO(O ₂)(gly) ₂ (Q)]	78	42.07 (42.26)	27.51 (27.69)	2.49 (2.66)	7.32 (7.46)
5	[UO(O ₂)(gly) ₂ (iso-Q)]	73	42.37 (42.54)	28.01 (28.17)	2.29 (2.51)	7.40 (7.69)
6	[UO(O ₂)(ala) ₂ (py)]	62	43.79 (43.99)	24.21 (24.39)	3.02 (3.14)	7.53 (7.76)

Figure in the parenthesis indicate the calculated values

Table 2. Physical properties of U(VI) complexes.

Complex No.	Complexes	Colour	Melting point ($\pm 0.5^\circ\text{C}$)	Molar conductance $\Omega^{-1}\text{cm}^2\text{Mole}^{-1}$	Magnetic Moment μ_{eff} (B.M.)
1	[UO(O ₂)(gly) ₂ (py)]	Pale yellow	>250	7.8	-0.539
2	[UO(O ₂)(gly) ₂ (2-pic)]	Light yellow	198	10.4	-0.522
3	[UO(O ₂)(gly) ₂ (4-pic)]	Pale yellow	192	1.9	-0.625
4	[UO(O ₂)(gly) ₂ (Q)]	Yellow	>250	5.7	-0.324
5	[UO(O ₂)(gly) ₂ (iso-Q)]	Yellowish green	>250	3.5	-0.426
6	[UO(O ₂)(ala) ₂ (py)]	Yellow	188	4.1	-0.725

Table 3. IR spectral data of U(VI) complexes.

Complex No.	ν (N-H) cm^{-1}	ν (C=O) cm^{-1}	ν (C-O) cm^{-1}	ν (M=O) cm^{-1}	ν (M-N) cm^{-1}	ν_1 (O-O) cm^{-1}	ν_3 ($\begin{matrix} \text{O} \\ \diagdown \\ \text{M} \\ \diagup \\ \text{O} \end{matrix}$) cm^{-1}	ν_2 ($\begin{matrix} \text{O} \\ \diagdown \\ \text{M} \\ \diagup \\ \text{O} \end{matrix}$) cm^{-1}
1	3197 br	1652 w	1576 m	903 vs	430 w	850 w	665 w	530 w
2	3202 br	1653 m	1584 s	809 s	433 m	797 m	668 s	523 w
3	3208 br	1683 w	1575 m	903 s	426 w	804 s	665 m	529 s
4	3235 br	1610 w	1560 m	918 s	-	849 s	655 w	510 w
5	3229 br	1575 w	1521 vs	936 vs	-	845 m	665 w	531 s
6	3240 br	1645 s	1508 w	921 vs	428 w	855 s	605 w	514 w

Related band intensities are denoted by vs, s, m, w and br representing very strong, strong, medium, weak and broad band respectively.

Table 4. Electronic spectral data of U(VI) complexes.

Complex No.	Complexes	λ_{max} (nm)
1	[UO(O ₂)(gly) ₂ (py)]	298, 345
2	[UO(O ₂)(gly) ₂ (2-pic)]	245, 315
3	[UO(O ₂)(gly) ₂ (4-pic)]	256, 345
4	[UO(O ₂)(gly) ₂ (Q)]	261
5	[UO(O ₂)(gly) ₂ (iso-Q)]	300, 340
6	[UO(O ₂)(ala) ₂ (py)]	255, 345

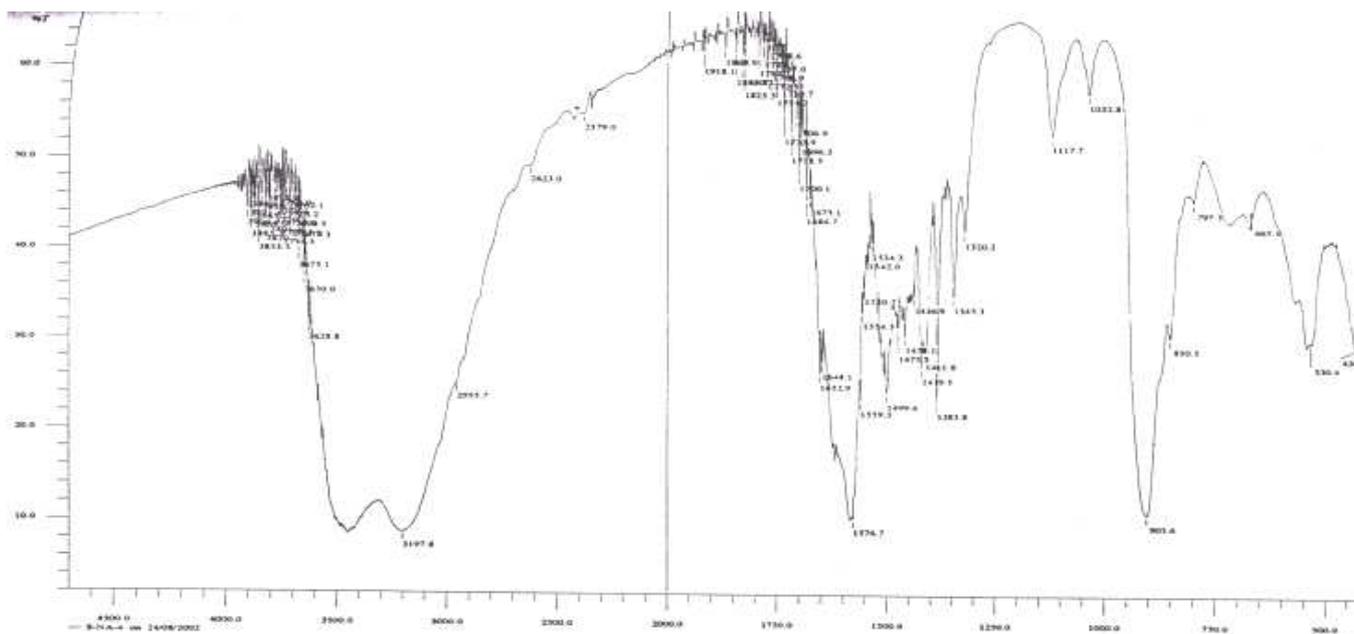


Figure 1. Spectral data of the complex [2] $[UO(O_2)(ala)_2(2-pic)]$.

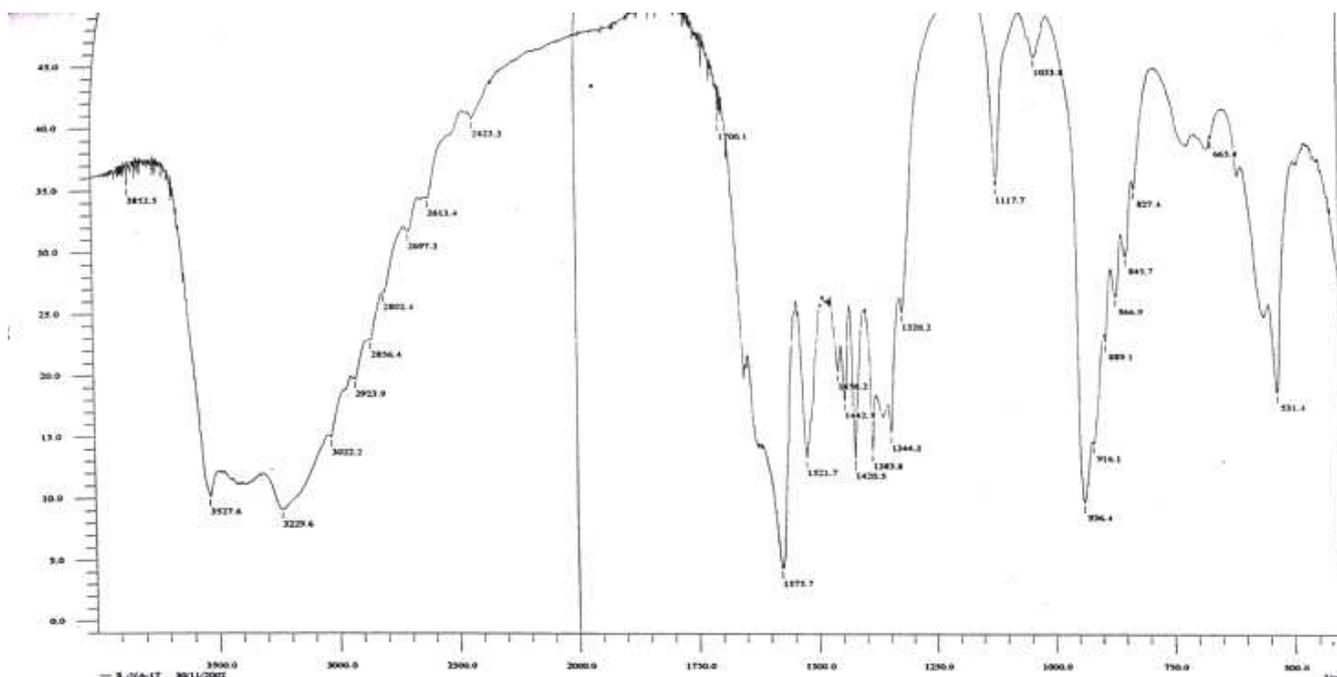
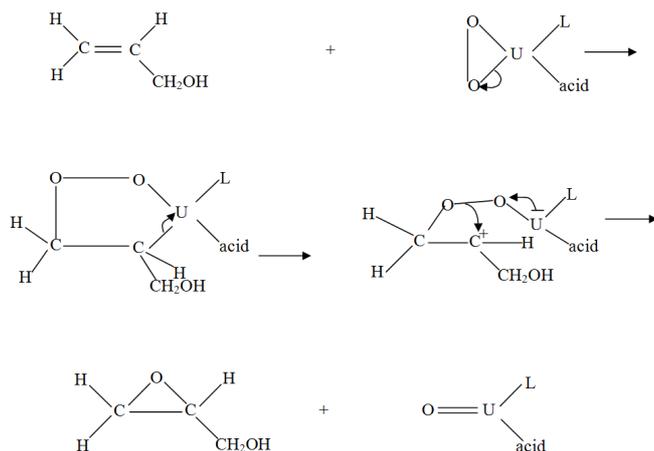


Figure 2. The infrared data of the complex 5 $[UO(O_2)(gly)_2(iso-Q)]$.

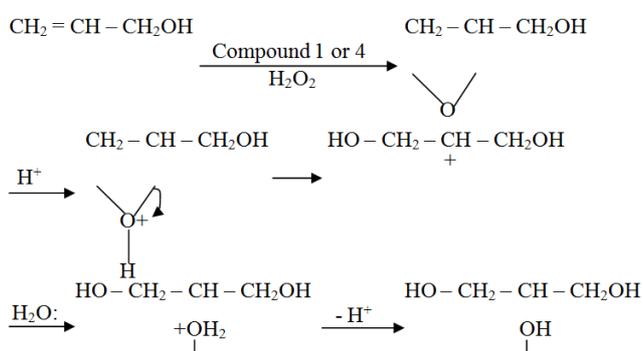
Reactivity: The present peroxy complexes were found to liberate iodine within 1-2 minutes on treatment with aqueous potassium iodide. Base on this observation, the possible reactivity of the complexes towards olefinic compounds could be explored. A stoichiometric mixture of compounds 4 and 5 with allyl alcohol did not exhibit any reaction. However, compound 6 reacts stoichiometrically with allyl alcohol (Reaction A) producing glycidol as indicated by IR band at 1060 cm^{-1} due to the C-O-C stretching mode [32, 33]. A possible reaction path is shown in scheme 1.

In reaction B, compound 6 was used to catalyze the oxidation of allyl alcohol by H_2O_2 and in this case the product

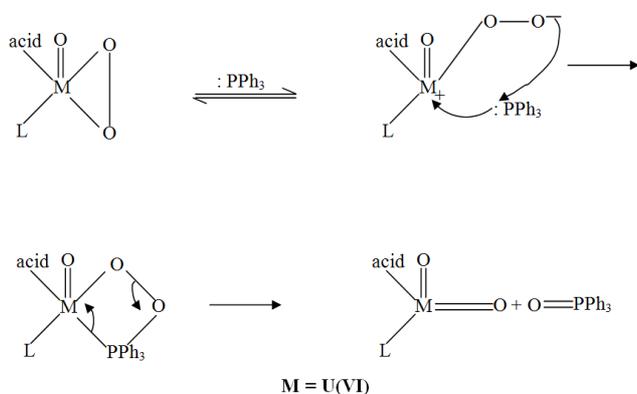
isolated was glycerol. The IR spectrum of this product was identical with that of an authentic sample. A possible reaction path is shown in scheme 2. The reaction C and D produced triphenylphosphine oxide and triphenylarsine oxide respectively. The products display IR bands at 1193 and 880 cm^{-1} due to $\nu(P=O)$ and $\nu(As=O)$ modes, respectively. The IR spectra of the residue of reaction C and D showed the disappearance of $\nu_1(O-O)$ bands which indicate the transfer of peroxy oxygen to the substrate. A possible reaction path is shown in scheme 3.



Scheme 1: A possible reaction path is shown



Scheme 2: A possible reaction path is shown



Scheme 3: A possible reaction path is shown.

On the basis of IR spectroscopic and other physical interpretation the molecular structure of (4) could be illustrated as shown in Figure 3.

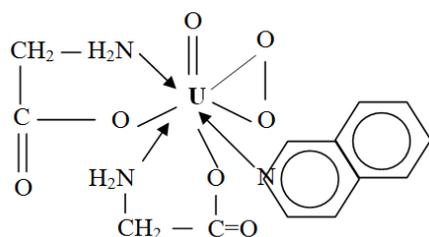


Figure 3. Proposed structure of complex (4). $[UO(O_2)(gly)_2(Q)]$.

4. Conclusion

It is concluded that the analytical data were in good agreement with the proposed empirical formulae of the complexes. The molar conductance values indicated the complexes are non-electrolytes in DMF revealing that the anions are covalently bonded in all the cases.

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